THE TREATMENT OF PLATINUM REFINERY WASTEWATER USING AN EVAPORATIVE CRYSTALLIZER

by

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Declaration

I, the undersigned, **Jabulani Luvuno (39044823),** hereby declare that the work contained in this dissertation has been produced by me without any collaboration with other students, staff or third parties aside from those acknowledged. I have not engaged in any acts of plagiarism and to the best of my knowledge, I have recognized all information obtained from other authors work. It is being submitted for the degree of Master of Science to the University of South Africa. It has not been submitted before for any degree or examination in any other University.

SIGNATURE DATE

(Mr)

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ABSTRACT

South Africa is a water scarce country. The expansion of the industrial, mining, and agricultural sectors to meet the needs of South Africa's growing population requires more water. There is therefore an urgent need to develop effective wastewater treatment processes in order to recover and reuse water. This dissertation presents the treatment of an acidic wastewater stream from a platinum refinery which at present is being disposed of by contract with a waste disposal company. The major concern in treating the acid effluent stream is the high concentration of sodium ions (18 200 mg/l) and chloride ions (104 900 mg/l).

The precipitation process is used to treat wastewater, but ultimately it generates more secondary waste as a sludge. The other process that is used to treat wastewater is reverse osmosis (RO). RO is usually preferred in the last stage of the treatment because the process is more expensive as membranes need to be replaced regularly. The approach used in this research focuses on evaporating liquid, consequently concentrating the remaining solution until the ions in the solution crystallize. The liquid produced is recycled back into the platinum plant for reuse, and the remaining salt crystals are collected as the useful product. The proposed water treatment process produces dilute hydrochloric acid as the condensate and a crystallized sodium chloride rich residue.

The refinery is currently disposing of around 20 000 l/day of wastewater to landfills. The proposed treatment process can recover half of the volume of the wastewater stream to the refinery, helping reduce the fresh water consumption of the process by 10 000 l/day. Furthermore, this will reduce the volume of wastewater going to disposal by a half, namely only 10 000 l/day will need to be disposed of.

The amount of Cl that can be recovered is variable and depends on the quantity of chloride in the wastewater. In the two samples processed the recovery was between a 2,5 w% and 10,7 wt% aqueous HCl solution. This corresponds to a saving of between 250 to 1000 kg/day of HCl. As the concentration of the recovered solution is variable, the recycling process would need to monitor the composition of the recycled stream and make up the acid concentration to some fixed value for reuse in the prices.

The production of a dilute hydrochloric acid stream should be particularly attractive to the platinum refinery as the operation of the refinery requires hydrochloric acid as a feed. Thus, by recycling the wastewater, the refinery would reduce the volume of wastewater to be disposed of thereby reducing the cost of disposal of the waste while simultaneously reducing the cost of buying fresh hydrochloric acid. The proposed recovery of liquid and recycling it back to the refinery, will also reduce the environmental impact of the refinery, and very importantly in a water scarce country, reduce the freshwater consumption of the process.

***Keywords**: Platinum Refinery Wastewater, Evaporative Crystallization, Recycling Water, Reducing Environmental Impact*

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Nomenclature

M_{to} is the initial mass of a solution.

M_t is the mass of the remaining solution.

$\sum M_s$ is the sum of the masses of samples of residue.

$\sum M_v$ is the sum of the masses of the collected distillate.

$C_{t,Na}$ and $V_{t,Na}$ are the initial concentration of sodium and volume of solution before the crystallization process respectively.

$M_{c,Na}$ is the total mass of sodium in the crystals formed.

$C_{f,Na}$ and $V_{f,Na}$ are the final concentration of sodium and volume of solution respectively at the end of the crystallization process.

$C_{i,Na}$ and $V_{i,Na}$ are the concentration of sodium and volume of individual samples of residue collected.

$C_{i-1,Na}$ $V_{i-1,Na}$ is the amount of sodium in solution at the beginning of stage *i*. $C_{i,Na}$ is the concentration of sodium in solution at the end of stage *i*.

$V_{i,Na}$ and $V_{si,Na}$ are the volume of the solution and the volume of sample of residue at the end of stage *i*.

$C_{t,Cl}$ and $V_{t,\,Cl}$ are the initial concentration of chloride (g/L) and volume of solution. M_{Cl} is the total mass of chloride in the crystals formed.

$C_{f,Cl}$ and $V_{f,Cl}$ are the concentration of chloride (g/L) and volume of solution at the at time t of crystallization process.

$C_{i,c}$ and $V_{i,c}$ are the concentration of chloride (g/L) and volume of condensate sample collected up to time t.

$\underline{H}_1$: the specific enthalpy of liquid water at 25 ^{o}C = 105 kJ/kg.

$\underline{H}_2$: the specific enthalpy of vapour at 102 ^{o}.

CHAPTER 1. INTRODUCTION

1.1 Historical background

In South Africa, fresh water is in short supply (Hedden and Cilliers, 2014) and it is categorized as a water-stressed country. According to the predictions published by the Department of Water and Environmental Affairs (DWAF) in 2008, the demand for water in South Africa will exceed capacity by 2025. Building more dams and large-scale water transport schemes is costly and will increase the demand on an already limited and stressed fiscus.

Reusing and recycling wastewater has been proposed as a potential solution to the water scarcity problem (Zbontar and Glavic, 2000). The large volumes of wastewater that are disposed from industrial and mining plants are not usable due to pollution. The most common metal pollution in fresh water comes from the mining companies. Faced with strict environmental regulations, nowadays heavy metals are the priority pollutants of surface and ground water. With the rapid development of industries, heavy metal wastewaters are directly or indirectly discharged into the environment. Many heavy metal ions, such as mercury, cadmium, lead, nickel, and chromium are known as very toxic. It is important to remove or reduce heavy metal contamination in order to prevent or reduce contaminating the environment.

Historically, pollution control meant end-of-pipe treatment; however, stricter environmental legislation and the high cost and relative ineffectiveness of this option has encouraged re-evaluation of pollution prevention strategies (Cervantes *et al.*, 2006). The application of pollution reduction techniques by industries results in reduction of compliance cost (King and Lenox, 2002). The South African government's regulations on environmental pollution apply not only to mining but to other manufacturing industries. The regulations impose strict limits on the levels of impurities in wastewater that can discharge into the natural environment.

Some of the wastewater treatment processes that are used to treat wastewater are reverse osmosis, precipitation, biological or chemical treatment, distillation, and crystallization. At the same time, the use of microalgal-based systems has been widely studied for a variety residual effluents treatment since the early 1950s. There are several advantages of nicroagal-based systems

compared to traditional wastewater treatment technologies, namely pollutants and pathogen decrease, nutrient recovery in the form of valuable biomass, energy savings, and CO_2 emssions reduction. In spite of all these advantages, there are still many challenges to overcome, such as land requirements, effect of wastewater characteristics, environmental and operational condition influence, and biomass harvesting and valorization (Molinuevo-Salces *et al.*, 2019).

Evaporative crystallization is energy intensive; hence it is important to improve energy utilization in the process. Many ways have been implemented to increase the efficiency of the evaporation processes such as multiple-effect evaporation, multi-stage flash, thermal vapour compression, and mechanical vapour compression and so on. In these processes, Mechanical Vapour Compression (MVC) is considered to be more economically efficient than conventional evaporation method as it provides a comparatively low cost (Lara, Osunsan and Holtzapple, 2011).

In MVC, a compressor pressurizes the vapour from the evaporator and this compressed vapour releases its heat by condensation to the evaporating liquid. The latent heat of the steam which would normally be lost, is thereby recovered. The system is compact, does not an external heat supplier, cooling water, and downstream condenser, therefore it is self- contained (Liang and Han, 2011).

1.2 Rationale of the Study

In order to avoid the environmental impact associated with the disposal of concentrated solution and sludge, it is desirable to achieve zero liquid discharge. Oxidation/reduction requires additional chemical, Climate sensitive, Energy intensive and Electrodes corrode over time (Barak 2010). For this, evaporative crystallization has emerged as a technical feasible alternative, which has already found industrial application. Although evaporative crystallization is known for being an energy-intensive process, some strategies are most commonly applied to reduce energy consumption, such as multiple stages or steam recompression. Residual energy sources may be used by conducting evaporation at temperatures as low as 50 ^{o}C by application of vacuum (Lu *et al.*, 2017).

1.3 Problem Statement

Mine wastewater treatment has often been linked to large capital cost, high operating expenses, and an open-ended liability for mine and process facility owners. A platinum refinery wastewater has a high concentration of sodium ions and excess chloride ions, which needs to be removed to render the water safe for either discharge into the natural environment, or for recycle. The choice of an appropriate wastewater treatment process or technology is dependent not only on the characteristics of the wastewater to be treated, but also on the costs involved in terms of energy consumption, operational expenses, and maintenance. A further challenge for mine and industry owners is that some of these processes can remove contaminants successfully, but generate a waste, such as sludge, which is difficult to dispose of, and thus requires further treatment. These factors should be taken into consideration when a plant adopts a wastewater remediation policy. A means of treating this wastewater will be investigated.

1.4 The aim and the objective of the research study

The main aim of this study is to investigate treating a platinum refinery wastewater using an evaporative crystallizer. The objective of the study is to efficiently remove sodium and chloride ions from platinum refinery wastewater and produce reusable water.

1.5 Research questions

The main aim is to treat platinum refinery wastewater using an evaporative crystallizer. The questions that will be answered are:

- What are the products of the process and what are the concentrations of these streams?
- How does the recovery and concentration of the product depend on the design and operation of the processes?
- Lastly how much energy is consumed in the process and how can the energy efficiency of the process be increased by the operation and design of the process?

1.6 Thesis outline

Abstract: Summarize the whole thesis and present all the major elements of the study in a highly condensed form

Introduction: Describe large problem to be solved

Literature review: Review the existing research in the problem area

Experimental method: Describe method followed to obtain the results

Results and Discussion: Present the findings and discuss their significance

Conclusion and Recommendations: Summarize the findings and make recommendations

CHAPTER 2. LITERATURE REVIEW

2.1 Introduction

Water is a scarce resource in South Africa (Otiene and Ocheng, 2004). The mining, power generation and industrial sectors in South Africa utilize 8 % of the total water demand, while 92% is supplied to Domestic, Urban and Agricultural sector, and as industrialization and economic growth continue this figure has been projected to more than double by 2030 (Department of Water Affairs, 2009). The drive towards sustainable development requires the industrial sector to evaluate its water needs and decrease the environmental impact of its activities. Industry uses various wastewater treatment processes to address the challenge of reducing water consumption and environmental impact.

2.2 Environmental consequences of industrial contaminants

The presence of both essential (such as, Copper, Iron, Zinc, and Manganese, which play an important role in biological systems) and non-essential metals (such as, Lead, Nickel, Chrome, and Cadmium) in the natural environment is of serious concern as elevated concentrations of metals may result in toxic effects on living organisms. The non-specific binding of metal cations to biomolecules contributes to the toxicity of metals, which results in the structural and functional modifications within cells (Marasinghe Wadige *et al.,* 2014).

The runoff of water from both urban and industrial may be contaminated with heavy metals and this has a negative impact on both plant and animal populations. Lead may result in the destruction of gastropods and fish; copper impacts the normal functioning of gastropods and molluscs; and cadmium, copper, lead, and zinc affect the survival of crustacea (Turki and Noori, 2013). An example of the negative impact of metals on the environment is the River Carnon in the UK, in which the only forms of animal life are those which have developed some tolerance to the metals being released through nearby mining (Rodríguez-Ventura *et al.*, 2008). Similar observations were made in the fish mortality profiles for the River Gwyddan, Wales, which receives water discharged

from a steel works. After an effluent treatment plant was installed, its beneficial effect on the survival of fish in the river was immediately observed Compton, 1997).

Food safety is also threated by metal accumulation due to the bioaccumulation of metals in animals (Wan Alwi et al., 2008). Slowly accumulating toxicity may manifest itself in several ways depending on the metal, metal species and the organism involved. In many cases, the reproduction of vertebrates and invertebrates is affected by metals. Furthermore, metals may affect the emergence success of eggs, activity, stress and nervous functions of vertebrates and the growth of both vertebrates and invertebrates (Compton, 1997). However, metals are not the only toxins released into the natural environment through industrial activities. Another major contributory group of pollutants is organic compounds. (Yang, Zhang, and Wang, 2015). There are many xenobiotic molecules, which are recalcitrant and are often highly toxic (Eleren and Alkan, 2009).

Organic chemicals present in concentrations below their solubility limit will occur in two forms in the environment, either mobile or stationery. The behaviour, transport and effect of the compounds depend on the pH, temperature, suspended solids concentrations and microbial activity in the system (Garcia *et al.*, 2016). Toxicity of these compounds varies greatly and includes carcinogenic and mutagenic effects and in some cases they may be lethal. The toxic and persistent nature of the compounds renders them a major concern and investigations into their environmental and physiological effects and degradation have been underway for many decades.

Not all compounds discharged into the environment through industrial activities are intrinsically toxic. In many instances the molecules, in the form of available carbon, nitrogen and phosphorus can be used as nutrients. Various industries, such as food processing, pharmaceutical manufacturing, fertilizer production, solid waste disposal and petrochemical refining dispose of these compounds into the environment (Carrera *et al.*, 2003). If these nutrients find their way into the environment, the concentration of phytoplankton and algae in the water increases rapidly; this creates eutrophication, a disruption in the functioning of the normal ecosystem and leads to hypoxic conditions that further degrade the quality of the water and functioning of the ecosystem.

Globally 25% of water is used by industrial sector (World Water Assessment Program, 2012), and given the growing strict regulations and limitations surrounding the use of water, industry in

developed countries has managed to reduce its water usage by 70 – 96% over the last two decades (Rahman *et al.*, 2012). This reducing in water consumption was achieved by a combination of process optimization, reduction, reuse, and recycling initiatives within organizations.

There are several factors involved in the final selection of treatment technologies, including economic, technical and specific local conditions. It has been realized that in many cases the same level of treatment can be achieved using different conventional and innovative technologies (Rahman *et al.*, 2012).

A number of management concepts have been developed for the minimization of water demand, wastewater discharge and associated costs. These concepts include water-pinch technology and advanced recycle technology. Water pinch analysis and wastewater minimization was initially designed as a process tool for heat recovery in the 1970s and the objective of the water pinch analysis was to minimize water consumption through maximizing the reuse of water (Mohammadnejad *et al.*, 2012).

Recycling and reuse are distinguished by the fact the recycled water may be returned to the original process, while reused water cannot be (Kuo and Smith, 1998). Direct reuse involves the use of wastewater from one process in another without any intermediate treatment steps. This can only be achieved if the contaminants from the first process have no effect on the second. The benefits of this system include the decreased use of potable water in the second process and lower wastewater discharge from the first. In all cases direct reuse should be considered first due to its low costs and simplicity followed by indirect reuse (partial treatment) and finally recycling (Feng and Chu, 2004). Recycling water involves the removal of some contaminants from the water, which is then returned to the same process. In many cases, this may be more difficult to achieve when compared to reuse as recycling may cause a build-up of contaminants (Mohammadnejad *et al.*, 2012).

In some cases, wastewater needs to undergo treatment before it may be reused. This is known as regeneration reuse (Mohammadnejad *et al.*, 2012). Two processes may be undertaken in this category. The first involves the separation of wastewaters into two streams. The stream with the lower contaminant concentration enters a regeneration plant and is treated to the quality required

for it to be used in another process. The stream with the higher contaminant concentrations enters a treatment plant where it undergoes treatment to meet discharge levels before being released from the site (Feng and Chu, 2004). This design requires two treatment facilities to generate both reuse water and wastewater of different qualities. Alternatively, one treatment facility services all the wastewater, treating it to different levels depending on whether reuse or discharge is the ultimate purpose for the wastewater (Feng and Chu, 2004). The latter is appropriate to this study, since the ideal outcome of optimization would be to have a zero-wastewater effluent process (Slatter *et al.*, 2009).

The technique of water pinch (Brouckaert, Buckley and Africa, 2000) can be used to analyse the water flows in a process and to identify opportunities for reducing consumption of water by recycling process water. The chief drawback of recycle technology is the difficulty of accommodating the practical constraints and characteristics of the water system. Multiple contaminants, flow rates and piping costs are just some of the variables which need to be considered when analysing and assessing the water usage. In addition, cost optimization is required to determine the benefits of implementing water pinch which requires mathematical programming techniques (Brouckaert *et al.*, 2008). At this point a holistic approach, combining several strategies and mathematical processes is needed to fully address the water usage of an individual industry and each application needs to be tailored specifically to the needs of the particular process (Wan *et al.*, 2008).

A wide range of technologies is available for the treatment of wastewater, depending on the quality and quantity to be treated and quality of product water required. Membrane and gravity separation, adsorption, centrifugation, chemical oxidation, evaporation, filtration, electro dialysis and biotechnologies have all been utilized with success in various industrial sectors (Ahmed *et al.*, 2017). A summary of the wastewater treatment technologies is presented in Table 2.1, showing their advantages and disadvantages. It shows the previous work that has been done using various technologies in wastewater treatment, and it provides challenges of each and every technology.

In the context of South Africa where there is a water shortage, the recovery of water from the chosen technology is an important factor in choice of technology. An evaporative crystallizer

reduces the quantity of material that needs to be to disposed of and produces a water stream that can be reused. It does not require extra pre-treatment, chemicals to be added or very complex technology. The technology is fairly energy intensive and if this could be optimized, this would make this technology attractive for this application. As shown in Table 2.1, the capex of the process is relatively low, operating costs are low and the process requires space. All of these would make evaporative crystallization an attractive technology for treating the wastewater from the refinery.

Table 2.1: Conventional metal recovery technologies and their associated advantages and disadvantages (taken from Barakat, 2011)

Process and range of operation	Advantages	Disadvantages	References
Ion exchange 10-100 mg/L or greater	High concentrating efficiency Ease of phase separation Resin may be regenerated to some extent No sludge Selectivity Simple and rapid	Expensive Sensitive to particles Resins eventually exhausted Pre-treatment required Limited availability of highly selective resins	Gomes et al, 2001 Ebbinand Gammon, 2002 Ahluwalia and Goyal, 2007
Chemical precipitation > 1000 mg/L	Low capex and operational expenditure Considered the simplest and cheapest means of removing heavy metals from solution Safe	Difficult metal separation Heterogeneous sludge in terms of metal content Large volume of wastewater to be treated Only effective for >1 g/L concentration	Kurniawan et al, 2006 Mauchauffee and Meux, 2007
Evaporation	Low capex and operational expenditure for atmospheric evaporation Reusable water recovered	Energy intensive Heterogeneous sludge produced Large space required	Cowan 1998
Solvent extraction	Selective Can be regenerated and reused	High chemical input required Expensive, sophisticated equipment required Generate wastewater	Gholivand and Nozori 2000 Bernadis et al. 2005 Cole et al, 2006
Coagulation/flocculation <100 mg/L or >1000 mg/L	Improved sludge settling and dewatering characteristics Sludge stability Bacterial inactivation	High operating cost due to chemical consumption High sludge volumes	Renault et al, 2009

2.3 Evaporative crystallization

Crystallization is the process of producing crystals from solution. In an evaporative crystallization, the solvent is evaporated, concentrating the remaining solution in solute, until the solution becomes saturated and crystals are formed. Despite its high energy demand, crystallization is an old technology that is still used today.

This separation process is important for industry because a large number of commodity chemicals, pharmaceuticals, and specialty chemicals are marketed in the form of crystals. The greatest disadvantage of evaporative crystallizer is that it produces a heterogeneous sludge as residue, which is difficult to separate to recover useful solids. This requires further separation processes of sludge or finding an alternative use of sludge, other than that disposal of sludge can be outsourced at a cost (Shen *et al.*, 2014).

2.4 Crystallization mechanisms

A solution is made up of a liquid (solvent), usually water, and one or more dissolved species (solute) that are solid in their pure form. The solubility is the maximum amount of solute that can be dissolved in a solvent at a particular temperature. Solubility varies with temperature, and in the case of most substances, the amount of solute dissolved increases with a rise in temperature (Schwartz and Myerson, 2002).

The supersaturation is created either by cooling or evaporating a saturated solution into metastable zone, resulting in the reduction of the amount of solvent available to hold the solute. Two phenomena compete for the crystallizing solute: crystal formation and crystal growth. The former is also called nucleation. Both nucleation and growth require that the solution be supersaturated; but there is a substantial difference in the rate dependence on the degree of supersaturation for the two processes (Randolph and Larson, 1971). Supersaturation is a measure of the actual quantity of solids in solution compared with the saturated or equilibrium solubility. It can be expressed by a number of methods:

- The ratio of actual solute concentration and the equilibrium concentration, C/C*
- The ratio of the difference between the solute concentration and the

equilibrium concentration to the equilibrium concentration, s =(C-C*)/C*

- The difference between the actual solute concentration and the equilibrium concentration, C-C*
- The difference between the system temperature and the equilibrium temperature, T-T* (Fernández González, Pedreira and Prieto, 2008).

Crystallization is distinguished from precipitation in that crystallization usually exhibit extremely high levels of supersaturation, primary nucleation, and low solubility. Figure 2.1 below explains the sequence of steps that lead to the formation of crystals.

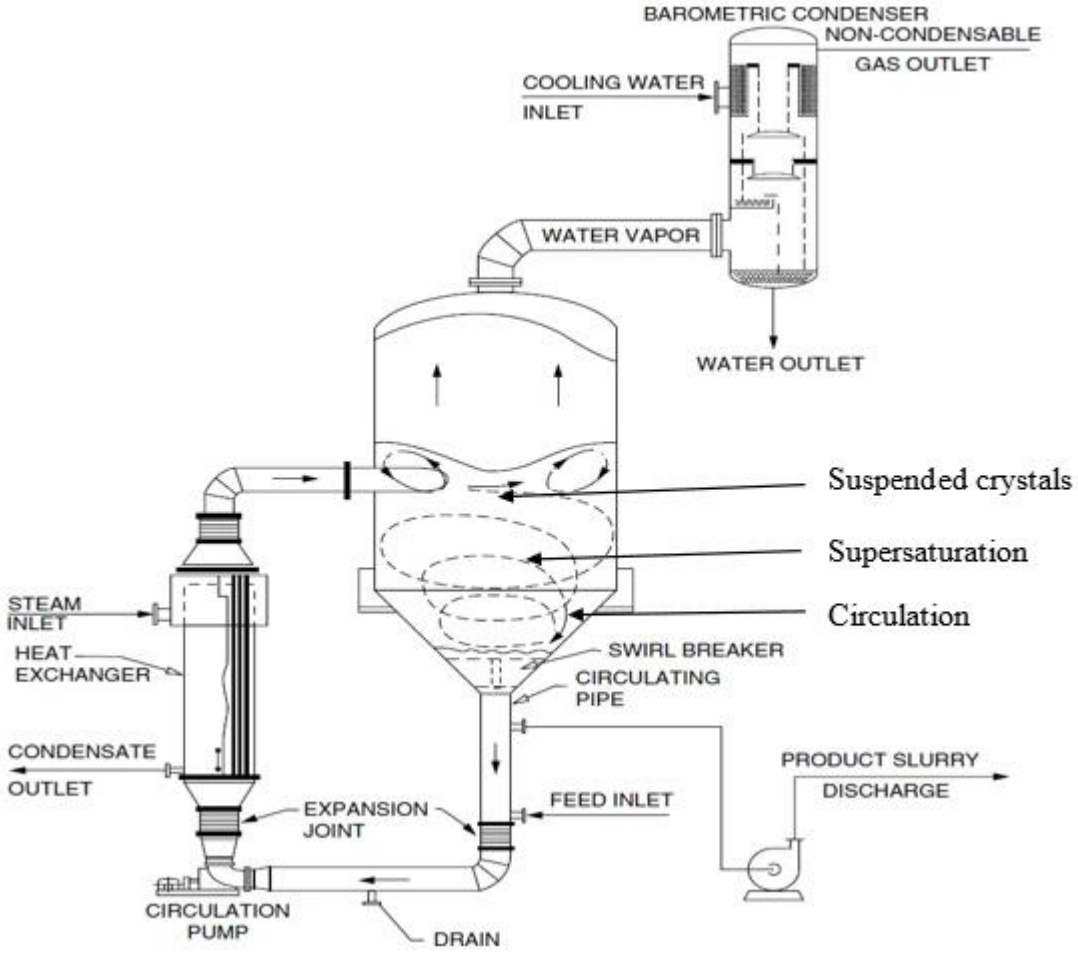

Figure 2.1: Diagram of a continuous forced circulation evaporative crystallizer (taken from Mullin, 2001).

There are three regions in the crystallizer, as labelled in Figure 2.1 above: These three regions are: Suspended crystals, Supersaturation zone and Circulation.

The processes occurring in these three zones are as follows:

- The region of suspended crystal: is a suspension where crystals are suspended in the solution and most of the crystal growth takes place in the crystallizer,
- The region of supersaturation: is the region where the solvent is removed from the solution which results in supersaturation under controlled conditions, and
- The region of circulation: is where the liquid is circulated throughout the system.

Understanding the dynamics and the processes occurring in the evaporative crystallizer enable better control of the crystal size distribution produced in the crystallizer. Batch crystallization is still widely used in the chemical industry due to its simplicity, flexibility and low cost. However, batch crystallization has many disadvantages, namely relatively high operation costs, long operation times due to shutdowns after every batch, poor reproducibility and broad crystal size distribution (Tung *et al.*, 2009).

When run in batch mode, the rate of energy transfer must continually increase throughout the batch cycle to maintain a constant maximum allowable level of supersaturation as the crystal surface area grows.

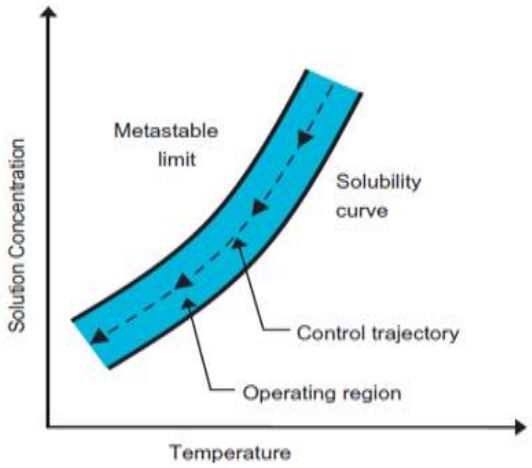

Figure 2.2: Operating region for batch crystallization defined by the solubility curve and metastable limit as function of temperature (taken from Wibowo, Wen-Chi and Ng, 2001).

Figure 2.2 above shows a schematic of the concentration–temperature profile of the process trajectory during crystallization. The trajectory lies in the region between the solubility and metastable limits and the trajectory chosen trades off the rates of nucleation and growth (Wibowo, Wen-Chi and Ng, 2001).

In the last few decades, advances have been made in the crystallization research area and new types of crystallizers have emerged (Wang *et al.*, 2017). Such developments include the transition of some crystallization processes from batch to continuous mode. Continuous processing is widely used nowadays since this mode of crystallization operation has the advantages of speed, low costs, and better reproducibility than the batch mode (Narducci, Jones and Kougoulos, 2011).

2.5 Operational issues of crystallizers

There are a number of operating issues which need to be addressed when designing and operation continuous crystallizers (Paroli, 2012). These include:

- Minimizing fouling in order to extend of operation cycle; crystals growing on heat transfer surfaces cause fouling and limit the heat transfer effectiveness.
- Maintaining crystallizer stability; a balance between crystal nucleation and grow need to be maintained in order to ensure that that particle size distribution of the solids is

acceptable.

- Separation of solids from the mother liquor; if the nucleation rate of particles is faster than the growth rate, this will, lead to smaller particles resulting in difficulties separating the solids from the liquor.

The evaporative crystallization process is energy intensive; multiple effects can be used to reduce energy demand. In addition, crystallization under vacuum may accelerate solvent evaporation at low temperature, however, capital expenditure (capex) is required for this process. There are fairly large heat effects in the crystallization of hydrated salts, However, in evaporative-type crystallizers, the heat of crystallization is usually negligible when compared with the heat of vaporization of solvent (Kamer and Dijkstra, 2000) due the energy intensiveness of evaporation.

2.6 Advantages and disadvantages of crystallization

There are a number of issues that need to be considered when deciding on using evaporative crystallization to treat wastewater. The solids can be recovered in a highly purified form and compounds can be obtained from relatively impure solutions by means of a single processing step. It can be performed at high or low temperatures, and it generally requires much less energy for separation of pure materials than other commonly used methods of purification, for example distillation (Motz, Mannal and Gilles, 2008).

While historic applications have been predominantly driven by the need to purify waste streams and to prevent further pollution in Europe, the dire shortage of water, coupled with a vibrant mining and metallurgical industry in South Africa, has provided impetus to extending applications on a direct business return basis as well. Crystallization helps in reclaiming valuable metals from wastewater rather than transferring them into waste. In many cases, the overall operating costs for environmental applications are outbalanced by the value of the recovered metals and the saving on waste disposal. Water treatment to reduce process water consumption is fast becoming a business necessity. Application of proven technologies in water balances provide an opportunity to turn what was previously a business cost into a cash positive and sustainable solution (Slatter *et al.*, 2009). This therefore leads to socio-economic benefits.

The disadvantages of evaporative crystallizers include high energy costs, long operation times due to shutdowns after every batch, poor reproducibility and broad crystal size distribution. This equipment can also not be used to crystallize organic compounds that are sensitive to high temperatures (Genck, 2003)

2.7 The treatment of the Platinum refinery wastewater

The use of conventional physico-chemical methods for treating industrial wastewaters can often result in complex process that only partially treat the wastewater, especially if the wastewater contains components which persist after the application of physico-chemical processes during production. In most cases these processes generate toxic, recalcitrant by- products which either requires further treatment or disposal.

The highly concentrated inorganic salt wastewater from the platinum refinery is currently disposed of by contractors, probably by disposing of in specially designated land fill sites. If the wastewater can be treated to recover and reuse some of the components of the wastewater, there would be environmental benefits as well as potential economic benefits. Currently, similar types of wastewater have been treated using evaporation techniques, such as multi-stage flash (MSF), multi-effect evaporator (MEE) and reverse osmosis (RO) methods. Among these techniques, MEE is considered to be more effective than the other processes (Zhao *et al.*, 2011).

The MEE method requires a large amount of external heating vapour, the system is complicated, and its operation is complex. Mechanical vapour re-compression (MVR) is an alternative method for the treatment of highly concentrated wastewater. The defining characteristic of MVR is the reuse of the energy of vapour produced in the evaporator (Alasfour and Abdulrahim, 2011). The advantages of MVR include: (1) a high thermodynamic efficiency; (2) compact equipment; (3) no requirement of an external heat source or condenser; (4) reliable and flexible operation; and (5) low-temperature operation (Aly and El-Fiqi, 2003).

This study will focus on treating a platinum refinery wastewater using an evaporative crystallizer. The quantity and composition of the liquid that can be recycled will be quantified. This will allow us to quantify the saving in makeup water and HCl consumption.

2.8 Conventional methods

Conventional methods for removing metals are either becoming inadequate to meet current stringent regulatory effluent limits or are increasing in cost. As a result, alternative, cost effective technologies are in high demand. Conventional techniques for removing dissolved heavy metals include chemical precipitation, carbon adsorption, ion exchange, evapourations and membrane processes (Gautam *et al.*, 2014). The selection of a particular treatment technique primarily depends on a variety of factors, e.g. waste type and concentration, effluent heterogeneity, required level of clean-up, as well as economic factors. The use of biological materials, including living and non-living micro-organisms, to remove and recover toxic or precious metals from industrial wastewaters has gained popularity over the years due to increased performance, availability and low cost of raw materials, microorganisms including bacteria. Algae and fungi and yeasts can efficiently accumulate heavy metal from their external environment (He and Chen, 2014).

The fundamental reason for the treatment of wastewater is to circumvent the effect of pollution of water sources and protect public health through safeguarding of water sources against the spread of diseases. This is carried out through a variety of treatment systems, which could be onsite treatment systems or offsite treatment systems. This section is therefore aimed at describing the offsite (activated sludge, trickling filters, stabilization ponds, constructed wetlands, membrane bioreactors) wastewater treatment system. All biological-treatment processes take advantage of the ability of microorganisms to use diverse wastewater constituents to provide the energy for microbial metabolism and the building blocks for cell synthesis (Cho *et al.*, 2013). This metabolic activity can remove contaminants that are varied as raw materials and by-products.

2.9 Activated sludge

The activated sludge is a process with high concentration of microorganisms, basically bacteria, protozoa and fungi, which are present as loose clumped mass of fine particles that are kept in suspension by stirring, with the aim of removing organic matter from wastewater. In recent years, biosorption has emerged as a cost-effective and efficient alternative for the removal of heavy metals from wastewaters (Azizi, Kamika and Tekere, 2016).

Many types of biomass in non-living form have been studied for their heavy metal uptake capacities and suitability to be used as bases for bio sorbent development. A review on biosorption of heavy metals by algal biomass was performed. These include bacteria, marine algae and others. Biosorption is a sorption process, where biomaterial or biopolymer is engaged as sorbent. The phenomenon of biosorption was observed in early 1970s when the radioactive elements (also heavy metals) in the wastewater released from a nuclear power station were found to be concentrated by several algae (Sheng, Ting and Chen, 2007). Early research conducted in laboratory studies had demonstrated that biosorption was a promising and cost-effective technology for the removal of heavy metals from aqueous solutions. Compared with conventional methods such as chemical reduction, ion exchange, precipitation, and membrane separation, biosorption technology possesses several advantages: low operating cost, high efficiency in detoxifying heavy metals that have lower concentrations, less amount of spent bio-sorbent for final disposal, and no nutrient requirements (Prajapati and Chaudhari, 2015).

The term bio refers to the life, which here means the micro-organism that can be potentially used to treat wastewater treatment. Several microorganisms were employed to remove nutrients and toxic chemicals. The employed biological methods were employed for treatment of sewage water (Rama Mohan, 2016). Twelve key factors were discussed including mineral diversity, nutrient reservoirs, steep gradients, high exchange rates, mesocosm structure, sub ecosystems, periodic and random pulses, cellular design microbial communities, photosynthetic bases, animal diversity, biological exchanges beyond the mesocosm, and mesocosm/macrocosm relationships.

The treatment of wastewater was studied using the different biological treatments and efficiency of those systems in removing the inorganic matter which serves as the nutrient for them. They are anoxic tanks, hydroponic tanks, and aerated tanks and algae tanks with planted sand filters. A combined treatment involving microbiological processes and hydroponics was given for treatment of domestic water. The treatment is found to be effective and the limitation is significant recycling of nitrogen and phosphorus through harvested biomass. The biological treatment especially fungi and bacteria for treating the wastewater especially the coloured compounds in the molasses-based distilleries effluents was studied. It was mentioned that the biological treatment along with enzymatic digestion is better and safe method when compared to other physical and chemical

treatments (Pant and Adholeya, 2007).

The effect of inhibitory of free nitrous acid on another metabolism of the wastewater is not studied. The information about microorganism's vital role was provided in removing the pollutants by consuming the inorganic nutrients in the polluted environment. The microbe cleans the pollutants by assimilation, consumption of organic material, and adsorption. It was mentioned that the biofilm formed by the microbes plays a major role in removing the heavy metals, organic matter, phenol, nitrates, pentachlorophenol, trichlorophenol, sulphates and quinoline. From the wastewater the natural foaming bacterial species were isolated and sequenced (Guo *et al.*, 2015). The factors that cause foam were also determined, and the role of bacteria in foaming and activated sludge formation was studied in depth.

The studies were carried out studies on the metal tolerance cyanobacteria Nostoc linckia and rivularis to grow in the sewage water and estimated its growth rate, its metal absorbance capacity and its cellular content. Nostoc rivularis was found to be effective in absorbance of the heavy metals by producing more metal binding protein. The details related to the status of cyanobacteria and difference between removal of cyano bacteria and bacteria and algae after absorption of heavy metals are found to be lacking in the study (Sood *et al.*, 2015).

2.10 Heavy metal treatment

A wide variety of active and inactive organisms have been employed as bio-sorbents to sequester heavy metal ions from aqueous solutions. It has been found that bio-sorbents are rich in organic ligands or the functional groups, which play a dominant role in removal of various heavy metal contaminants. The important functional groups are carboxyl, hydroxyl, sulphate, phosphate, and amine groups. As heavy metals are non-biodegradable, clean-up of contaminated water and soil is rather challenging. It is an emerging need to develop cost-effective technologies that can remove heavy metals from contaminated soil and water (Zakhama, Dhaouadi and M'Henni, 2011).

The currently practiced contaminated water and soil technologies are precipitation, adsorption, reduction, coagulation, and membrane filtration. Their performances are generally acceptable; however, they have several drawbacks. In particular, they cannot work very well in treating heavy

metals, particularly when concentrations are very high. Sorption process has been extensively used to remove toxic metals from aquatic medium using low-cost adsorbents such as agriculture wastes and activated carbon developed from agriculture wastes. Among the most promising biomaterial is algal biomass (Mack *et al.*, 2011). The presence of carboxylic (–COOH), sulfonic (–SO3H) and hydroxyl (–OH) groups in the marine algae polysaccharides is observed to be responsible for impressive metal uptake by marine algae.

Moreover, the macroscopic structures for marine algae present a convenient basis for the production of bio-sorbent particles suitable for sorption process. A New method was proposed for treating industrial heavy metal water treatment using algae. From the study the doubt arises whether pre-treatment is necessary to make algae as bio-sorbents. The oil extraction was developed from algae waste which was activated by alkaline treatment to remove the cadmium II in batch and column studies. Various models like Langmuir, pseudo second order isotherm, Thomas, Adams, and Yoo–Nelson were used to describe the kinetic models of batch and columns respectively. The treated algae are found to be efficient in removing cadmium II. The limitation is treatment with alkaline, which is difficult for industrial process. The Azolla was made as biosorption material by chemical modification and tested to remove the Cs and Sr solutions. The toxicity of those metals in normal algae growth was studied. Micro particle induced X ray emission and FTIR were used to study the absorption isotherm. A new method for chemical mapping at atomic level micrometre size level was used (Mashkani and Ghazvini, 2009). The best result was obtained at pH 8.8. Even though the results are encouraging every time chemical modification is quite difficult at industry level.

Absorbance isotherm was estimated using Langmuir model. The ability of both activated carbon and normal algae in natural, synthetic sea water and wastewater was also estimated. Both dried algae and activated carbon are found to absorb the toxic chromium at high pH. They are promising in removing toxic chromium from all types of water and different solutions but obtaining dry powders and activated carbon is not found to be efficient method. The limitation of the study is with recycling, which is not possible and biomass production (He and Chen, 2014).

The efficiency of the immobilized biocers was tested for absorbance of nickel, chromium, copper

and lead in drinking water. The structure of biocers was analysed by SEM and light microscope. The gels have good mechanical strength and have high capacity to absorb the metals in gel condition. Hence it is the easy and cost-effective method. The limitation of the study is recycling, which is not possible and biomass production. The macro brown algae Undaria pinnatifida was made into chars by both physical and chemical methods and used to absorb the copper metals in solution (Cho *et al.*, 2013). The absorption isotherm was studied using pseudo second order kinetic models; even small amount has highest capacity to absorb the metals at low concentration. It is not applicable to industrial scale because of slow growth of macro algae and its process into chars requires more equipment, leading to uneconomical.

The biomass was cultured in the artificial stream wastewater. The biosorption of the metals was estimated and modelled using Langmuir isotherm. The dried biomasses in the batch experiments are observed to be efficiently good in removing the copper and cadmium at maximal rate which shows that microbial biomass has high affinity for metals. The biomass immobilization is not efficient and promising method for treatment (Zhu *et al.*, 2015). Treatment using live algae and bacteria forms is the alternative.

CHAPTER 3. EXPERMENTAL METHODS

3.1 Introduction

The analysis of the wastewater that was obtained from the platinum refinery is presented in this chapter. For this, the synthetic mixture was made to approximate the wastewater that was used for calibration and testing of the experimental batch evaporative crystallizer. In addition, the analytical techniques used to analyse the composition of the water samples and the laboratory apparatus that were used for the evaporation and crystallization tests are discussed.

3.2 Composition of synthetic wastewater

A synthetic wastewater mixture was prepared to be used as a surrogate for the refinery wastewater using a mixture of hydrochloric acid, sodium chloride and water. This solution was used to test if the presence of other components in the wastewater had an impact on the boiling curve and crystallization of the solution. The synthetic solution was made up of 14g of 32% w/w HCl: 23 g NaCl and 463 g of distilled water. This gave a solution with 104910 mg/l of Cl^- and 18231 mg/l of Na^+ ions.

3.3 Apparatus use for evaporation and crystallization tests

The experiments were conducted using a three-neck round flask with a magnetic stirrer and fitted with a condenser and a thermometer. A heating mantle at 100 ^{0}C as the set point temperature was used to supply energy to the system (see Figure 3.1). When 50 ml of condensate had accumulated, 10 ml of residue sample was taken for analysis.

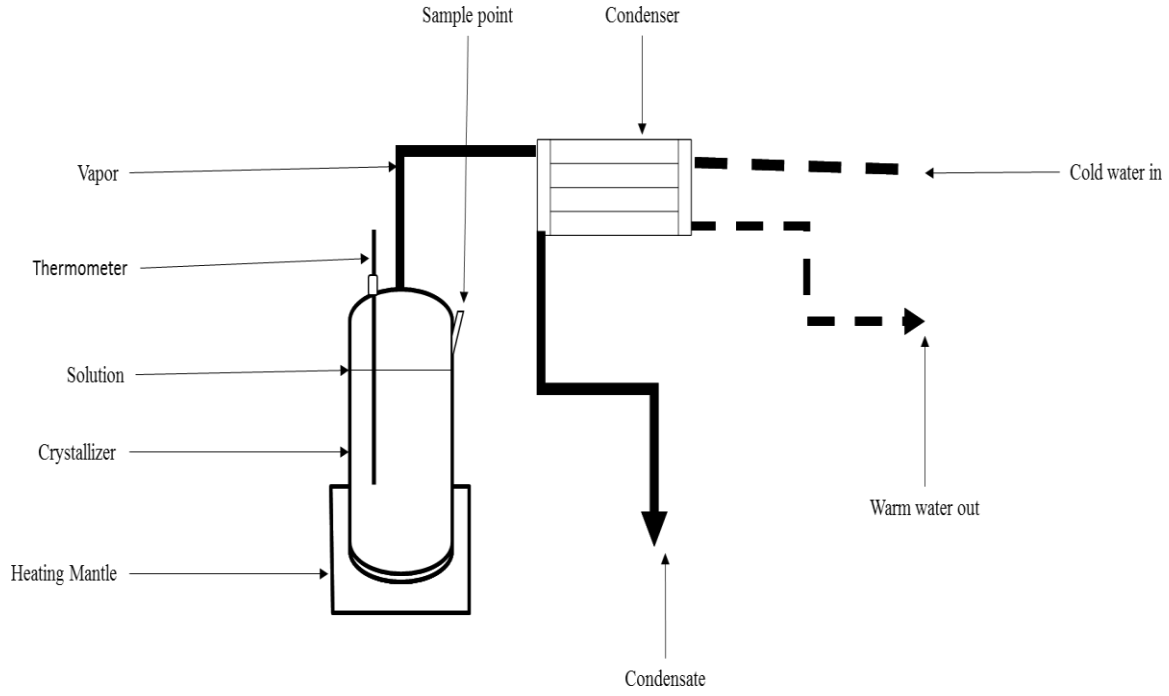

Figure 3.1: Schematic representation of the evaporative crystallizer used in the laboratory tests.

3.4 Methodology

500 ml of wastewater was placed in the flask and heated to boiling point. The vapour from the flask was condensed and collected in a graduated 100 ml measuring cylinder. When 50 ml of condensate had accumulated in the measuring cylinder, 10 ml of the concentrated residue from the flask was also collected. Thus, the residue was sampled at equal quantities of condensate collected. The time and temperature of the residue was recorded when the samples were collected, that is when aliquots of 50 ml of condensate had been recovered.

The samples were collected until the solution in the flask became so viscous that sputtering occurred and salt crystals where deposited on the glass. At this stage it was not possible to ensure that sample of the residue in the flask was representative. This occurred when around 300 ml of condensate had been collected, or around 200 ml of residue remained in the flask. Repeat runs on the wastewater were done to check the reproducibility of the experimental procedure.

3.5 Analytical Methods

3.5.1 Atomic Absorption spectrometry

The residue sample was analysed three times to measure the accuracy of the results for sodium and chloride ion concentration, using an Atomic Absorption Spectrometer (AAS) (Perkin Elmer Analyst 200) and Spectroquant Pharo 300, respectively. The sample concentration of each sample was averaged as reported in Table A 2 to Table A5 in Appendix A.

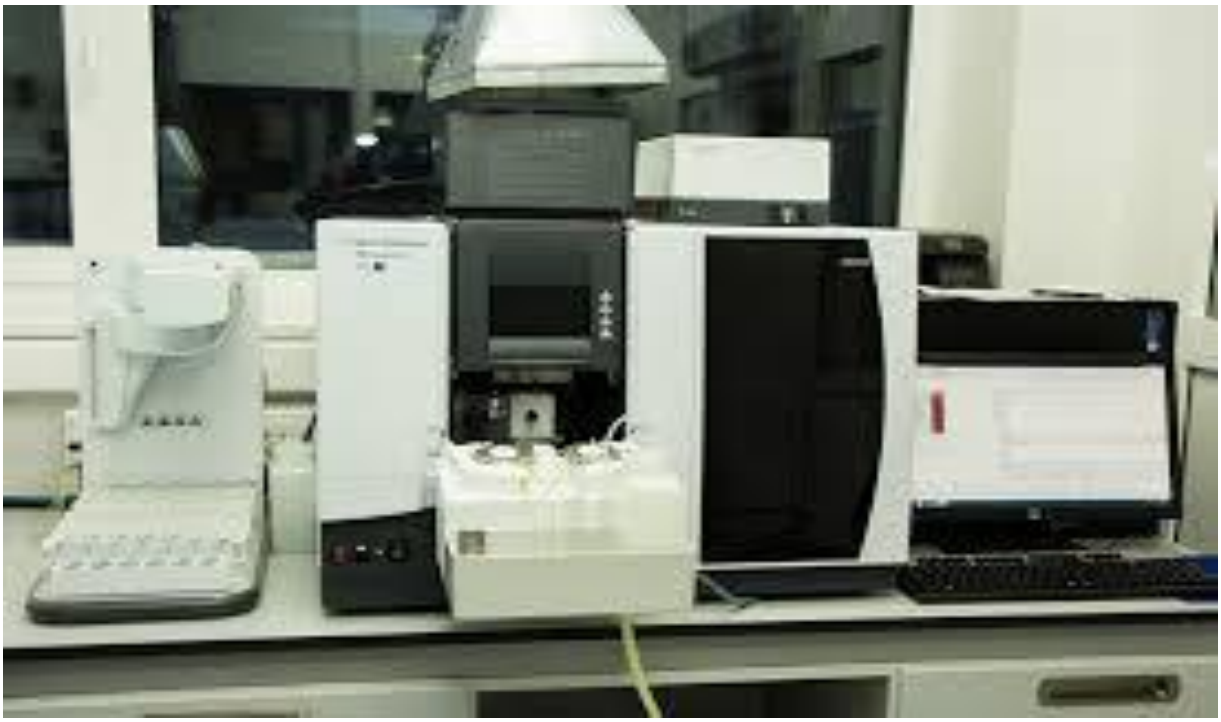

Figure 3.2: Atomic Absorption Spectrometry.

Atomic absorption spectrometry (AAS) measures the concentrations of elements. It makes use wavelengths of light specifically absorbed by an element. AAS is so sensitive, such that it can measure down to parts per billion (µg dm–3) in a sample. Atoms of different elements absorb characteristic wavelengths of light. Sample is analysed to see if it contains a particular element using light from that element. In AAS, the sample is atomised and converted into ground state free atoms in the vapour state, and a beam of electromagnetic radiation emitted from excited element atoms is passed through the vaporized sample.

The acetylene gas flame lean blue was used as an oxidizing agent. The flame is the source of thermal energy that makes sample atoms to undergo transition from the ground state to the first excited state. The instrument was calibrated using three commercialized sodium standards, 25 mg/L, 50 mg/L, and 100mg/L, respectively. These standards were chosen because the solution samples were highly concentrated. The solution samples were 1000 times diluted with deionized water for the instrument to be able to read them. The dilution of the samples was done in two separate steps. Step 1: Added 10 ml of sample to 200 ml flask and then filled with deionizedwater. Step 2: Took 5ml of the latter solution and added into 250 ml flask then filled with deionized water.

A sodium lamp was installed, then element Na was selected on the instrument. Lamp current was set to 12, wavelength 589 nm, and read delay to 5 seconds, and the lamp flame achieved was blue. The calibration was done with a blank and the three sodium standards. The calibration curve is shown in Figure 3.3. The calibration curve was linear with a regression correlation of 0.99.

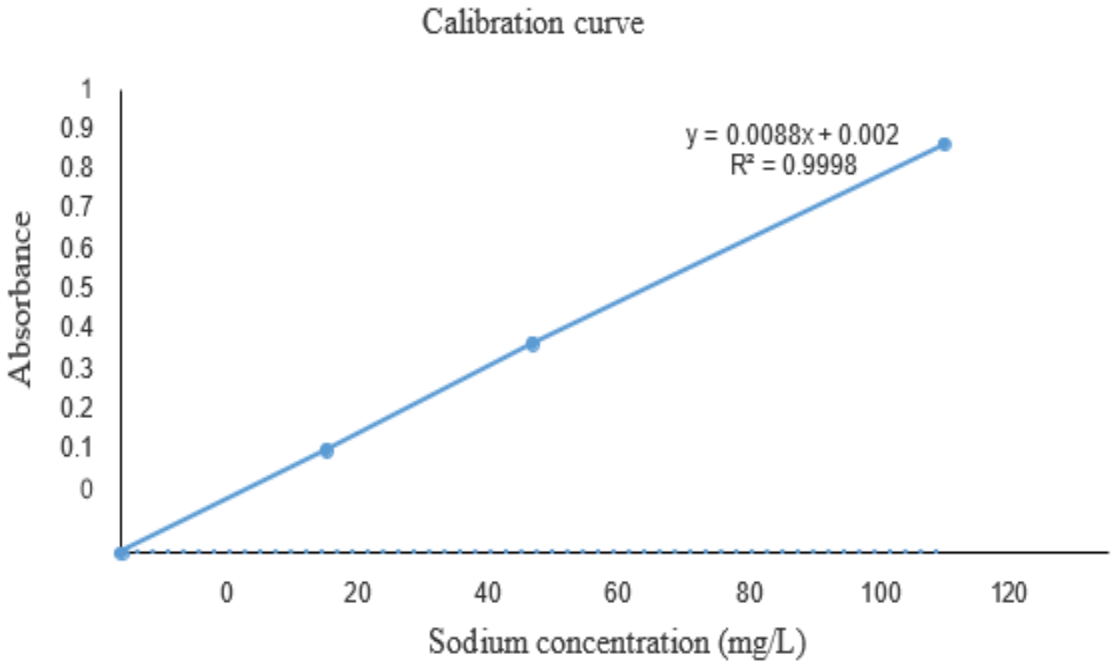

Figure 3.3: Atomic absorption spectrometry calibration curve for sodium.

Figure 3.3 was obtained using sodium standards of known concentrations. It shows that absorbance is directly proportional to the concentration of the analyte absorbed for the existing conditions. The concentration is determined from a calibration curve. The linear calibration shows that the

actual sample analysis results will be reliable and accurate.

3.5.2 Spectroquant Pharo 300

Figure 3.4: Spectroquant Pharo 300.

The Spectroquant Pharo 300 with a wavelength of 190-1100 nm is an instrument for all purpose. It is suitable for measurements of preprogrammed methods with Spectroquant Test Kits or programming of own methods. No matter whether you're using a 16 mm round cell or a 10, 20 or 50 mm rectangular cell in combination with the AutoSelector: all types of cell are automatically identified by the Spectroquant® Pharo and the correct measuring range is selected accordingly. No time-consuming search for the matching adaptor, no more errors when entering the correct method number – mistakes are fully excluded.

The Spectroquant was used to measure chloride ions concentration in both the solution and the collected distillate. The Spectroquant used Chloride test kit. Method: 10-250 mg/LCl^{-1}

Spectroquant for chloride ions analysis. The concentration of the solution under investigation was too high in that it lay outside the measuring range of the instrument. In this case samples had to be diluted 1000 times to be within the aforementioned range. The dilution of the samples was done in two separate steps. Step 1: Added 2ml of sample to 200 ml with distilled water. Step 2: Took 5ml of the latter solution and made up to 50 ml.

Carrying out the calibration the method was selected manually from the Specrtoquant Zero Adjustment Blank, Subsequently, correct chloride measuring ranges from 10 – 250 mg/L was selected. The calibration was done with the blank and chloride standards. The calibration curve is shown in Figure 3.5. The calibration curve was linear with a regression correlation of 0.99.

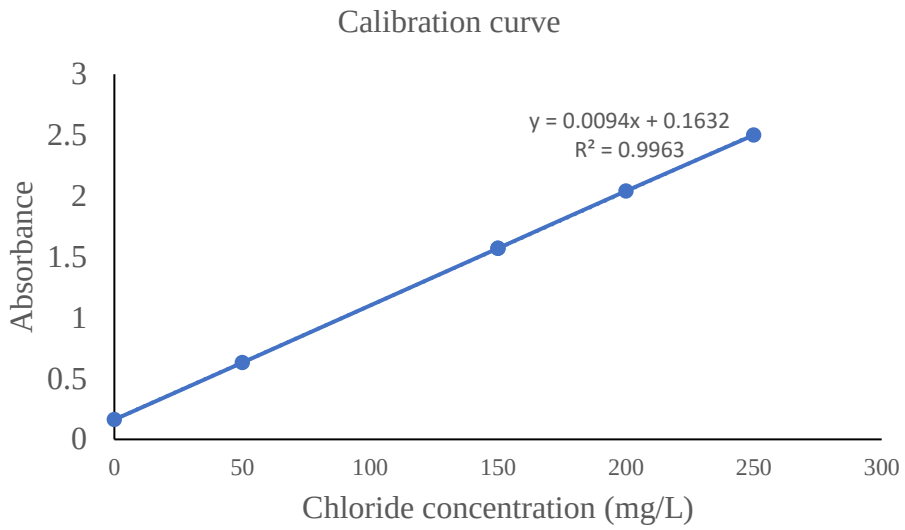

Figure 3.5: Spectroquant calibration curve for chloride.

CHAPTER 4. RESULTS AND DISCUSSION

4.1 Introduction

This chapter gives a detailed discussion of the results from the experiments conducted, as explained in detail in Chapter 3. The results and analysis are shown in both graphical and tabular form.

4.2 Results and discussion

The full wastewater analysis in given in Appendix A, Table A 1. This analysis was done by an independent laboratory called Setpoint Laboratories and ICP-OES was used for wastewater sample analysis. From the data, it can be seen that the major contaminants in the waste are sodium (18 231 g/l) and chloride ions (104 910 g/l) with iron being the next highest at 4000 mg/l and sulphate at around 200 mg/l. The research concentrated at looking at the removal of sodium and chloride ions from the wastewater. A summary of the major components in the wastewater is given in Table 4.1

Table 4.1: Summary of composition of the major components in the effluent from platinum refinery wastewater sample 1

	Concentration (mg/l)
pH <**0.2**	
Chloride ions	104 910
Total Dissolved Solids (TDS) at 180^{O}C	81 860
Sodium ions	18 231
Iron	4008
Sulphate	236

The quantity of waste produced by the refinery is confidential. In order for us to realise the impact of water recovery, the study was based on a (fictitious) quantity of 20 000 L/day of platinum refinery wastewater. Thus, the quantities of the major components in the wastewater are as given

in Table 4.2 below

Table 4.2: Quantities of refinery waste disposed of daily based on our case study on a fictitious quantity

	Concentration		Quantity
	(mg/l)	(mol/l)	(kg/day)
Water			20 000
Chloride ions	104 910	2,96	2 098
Sodium ions	18 231	0,79	365
Total Dissolved Solids (TDS) at 180^{o}C	81 860		1 637

If the amount of water disposed of can be reduced by reclaiming and recycling the wastewater, then this would result in less make up water being used by the refinery, which in a water stressed country is very important. This also means that the environmental impact of the process would be reduced in two ways; firstly, by less material being disposed of to waste disposal sites and secondly, by reducing the freshwater requirements of the process.

4.2.1 The solubility curves and reproducibility of the results

From the full analysis of the platinum refinery wastewater (sample 1) given in Table A.1 Appendix A, the wastewater had some other minor salts and metals but contained mainly sodium chloride as a crystallizable component.

The platinum refinery wastewater was heated and the condensate collected as described in Chapter 3. Three repeat experiments were performed for this wastewater and the results are given in Table A 2 to Table A 4. The results shown graphically in Figure 4.1 (concentration of sodium versus time), Figure 4.2 (temperature versus time) and Figure 4.3 (concentration of sodium versus temperature).

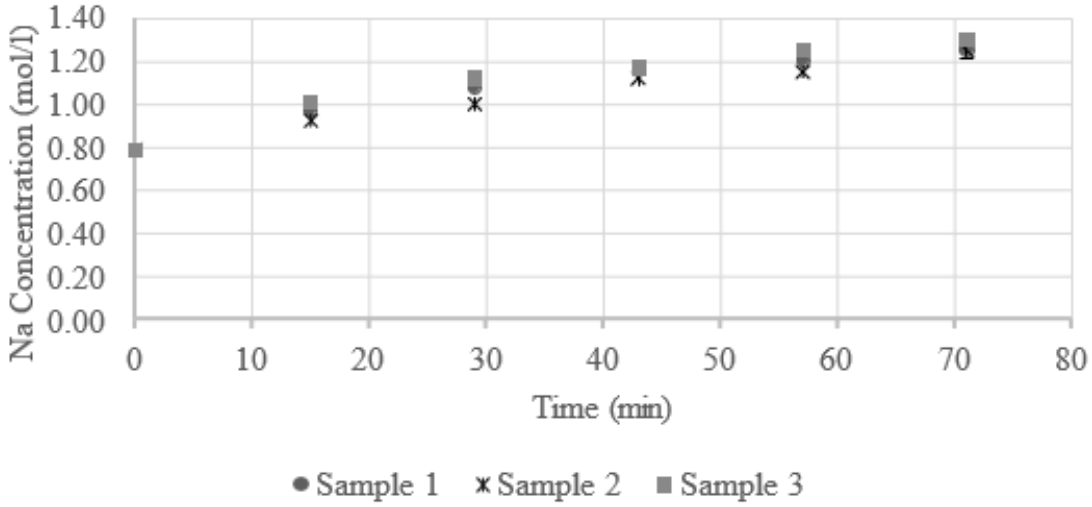

Figure 4.1: Graph of sodium concentration in the residue in the batch crystallizer vs time for three repeat runs on the platinum refinery wastewater (sample 1).

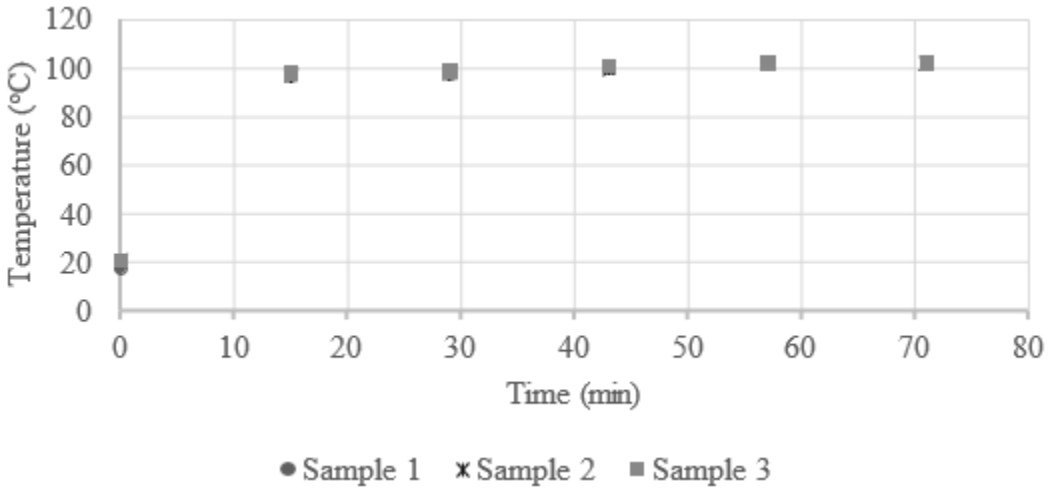

Figure 4.2: Graph of temperature in the residue in the batch crystallizer vs time for three repeat runs on the platinum refinery wastewater (sample 1).

Figure 4.2 above shows that temperature gradually increases with time and after 10 minutes then it becomes constant because the solution has reached its boiling point. This indicates the maximum achievable saturation of the solution at this constant temperature.

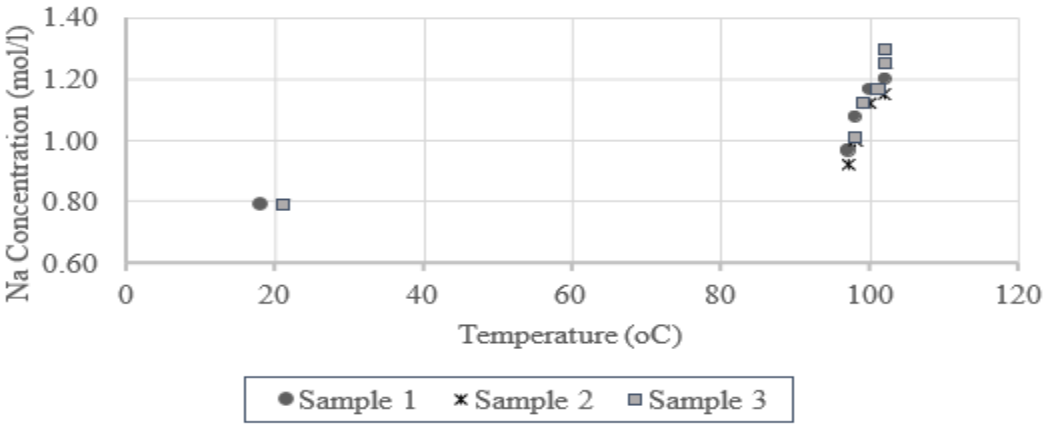

Figure 4.3: Graph of sodium concentration in the residue in the batch crystallizer vs temperature for three repeat runs on the platinum refinery wastewater (sample 1).

Figure 4.3 above shows that temperature has a clear effect on Na concentration, because Na concentration increases with increasing temperature. To see if the presence of the other species in the wastewater had any significant effect on the boiling characteristics of the wastewater, a run with the synthesized solution of salt, hydrochloric acid and water was done. The experimental results for the synthesized solution with evaporative crystallizer are given in Table A.5 in Appendix A and the results are shown in Figure 4.3 and Figure 4.4.

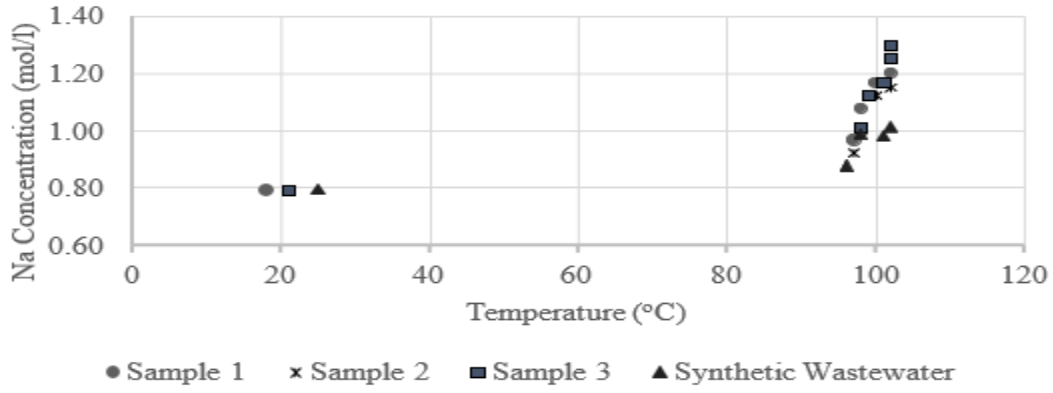

Figure 4.4: A comparison of the measured sodium concentration in the liquid residue for batch experiment vs temperature. Three repeat runs were performed on the refinery wastewater (sample 1) and one on the synthetic wastewater.

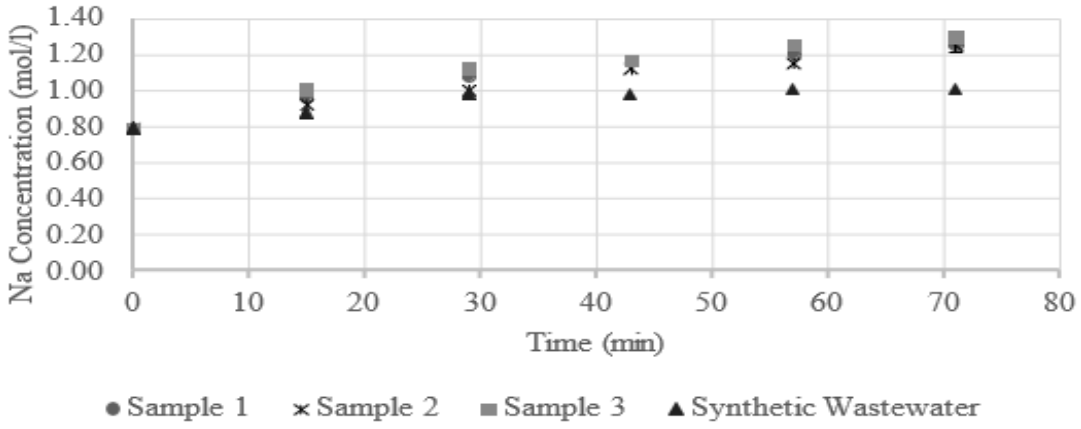

Figure 4.5: A comparison of the measured concentration of sodium in the liquid in the residue for a batch experiment with respect to time. Three repeat runs were performed on the refinery wastewater (sample 1) and one on the synthetic wastewater.

Figures 4.4 and 4.5 show the sodium concentration in the boiling liquid in both the refinery wastewater as well as the synthesized wastewater as a function of temperature and time respectively, and it can be that the different wastes behave relatively similarly. This suggests that the effects of the other species in the wastewater do not make a large effect on the boiling behaviour of the solution and that when analysing the results, and other species were neglected.

Comparing the results in Figure 4.4 and 4.5 shows that the experimental results have a reasonably high degree of reproducibility. It can also be seen that the temperature reaches 97 ºC fairly quickly and then slowly approaches 102 °C. The latter constant temperature is considered as a boiling point of platinum refinery wastewater. From Figure 4.5 it can be seen the concentration in the residue approaches 1,3 mol/l as the temperature tends to 102 ˚C. The literature value for a saturated salt solution at its boiling point is 108,7 ˚C and the solubility is around 6,8 mol/l. Thus, the solubility of NaCl in the wastewater (1,3 mol/l) is much lower than in a plain salt solution.

A soluble ionic compound dissociates into two ions in solution. For example, when an ionic substance like sodium chloride is added to water, it dissociates into sodium and chloride ions e.g., $NaCl\ (s) \rightleftharpoons Na^{+}\ (aq) + Cl^{-}\ (aq)$. The addition of either of these two ions (from a compound or solution with an ion in common) will decrease the solubility of the compound with lower solubility. In the case of a mixture of HCl and NaCl, the NaCl has lower solubility. According to Le

Chatelier's principle, the addition of chloride ions from HCl will stop the ionization of sodium chloride and shift its equilibrium to the left (Boyd, 2015), thereby reducing the solubility of NaCl in aqueous HCl solutions.

4.2.2 Mass balances

When designing a crystallizer mass and energy balances there are important factors for design and analysis purposes. These factors provide means for sizing equipment and the set of operating conditions that incorporate an element of economics in the procedure. The mass balance can be used for both analysis and synthesis and in particular it can be used to estimate the yield of crystals in batch crystallization (J. Mullin, 2001).

4.2.2.1 Overall mass balance

The mass balance was done on the average of the three runs for the platinum refinery wastewater. It was assumed that no solution was lost during the experiments. All the samples that were taken were measured and weighed. The volumes of the condensate samples were 50 ml each, and upon weighing them proved to weigh exactly 50 g, while the 10 ml solution samples from the crystallizer were heavier than 10 g by 0.203 g, 0.205 g, 0.213 g, and 0.215 g respectively. This variation was taken to be negligible. The averaged sodium concentration of the data in Appendix A is given in the table below.

Table 4.3: The averaged concentration data for the platinum refinery wastewater experiments (sample 1)

Volume Residue	Temperature	Time	Sodium Concentration in Residue	
ml	^{0}C	min	(g/l)	(mol/l)
500	18	0	18,2	0,79
440	97	15	20,3	0,88
380	98	29	22,7	0,99
320	100	43	23,8	1,04
260	102	57	24,6	1,07
200	102	71	27,5	1,19

The overall mass balance becomes:

$$M_{t^0} = M_t + \sum M_{ir} + \sum M_{ic} \quad 4.1$$

Where: M_{t^0} is the initial mass of a solution

M_t is the mass of the remaining solution

M_{ir} is the mass of the sample of residue collected

M_{ic} is the mass of the sample of collected condensate

Equation 4.1 can be rearranged to calculate the solution remaining in the crystallizer as follows:

$$M_{t^0} = M_t + (\sum M_{ir} + \sum M_{ic}) \quad 4.2$$

Table 4.4: ^{t} Overall balance for the wastewater crystallization process. The data is the average of the three runs on the platinum refinery wastewater. The density of the solution is assumed to be 1 kg/l.

Time	Condensate Samples		Residue Samples		Residue Solution	Total Volume
	Volume	Cumulative volume of condensate samples	Volume	Cumulative volume of residue samples	Volume	
min	l	L	l	l	l	l
0.00					0,50	0,50
15.00	0,05	0,05	0,01	0,01	0,44	0,50
29.00	0,05	0,1	0,01	0,02	0,38	0,50
43.00	0,05	0,15	0,01	0,03	0,32	0,50
57.00	0,05	0,2	0,01	0,04	0,26	0,50
71.00	0,05	0,25	0,01	0,05	0,20	0,50

During the crystallization process, the sample of residue solution was taken, and condensate collected. When the experiment was completed the total mass of the condensate collected was 250

g, total mass of residue sample solution collected 40 g, and the residue which was a viscous solution containing crystals remaining in the crystallizer was 200 g. When these masses were added together, they totalled 500 g which is the initial mass of the feed used for the experiments.

4.2.2.2 Mass balance on sodium

For this study, it was imperative to determine the mass of crystals formed during the experiment. The amount of salt crystals was determined by doing a sodium balance. If it is assumed that no crystals were collected in the 10 ml samples of residue that were collected. Therefore, then the total amount of sodium before the crystallization process must be equal to the sum of the amount of sodium in the crystals formed in the boiling flask; the amount of sodium remaining in the residue solution after the crystallization process; and the cumulative amount of sodium collected in the samples of residues.

This can be expressed as follows:

$$C_{t^0} V_{t^0} = M_{c,Na} + C_{r,Na} V_r + \sum C_{ir,Na} V_{ir} \quad 4.3$$

Where:

C_{t^0} and V_{t^0} are the initial concentration of sodium and volume of solution before the crystallization process respectively;

$M_{c,Na}$ is the total mass of sodium in the crystals formed in the boiling flask;

$C_{r,Na}$ and V_r are the concentration of sodium and volume of residue solution respectively.

$C_{ir,Na}$ and V_{ir} are the concentration of sodium and volume of the individual sample of residue collected;

Equation 4.3 can be rearranged to calculate the number of crystals formed as follows:

$$M_{c,Na} = C_{t,Na} V_{t^0} - (C_{r,Na} V_r + \sum C_{ir,Na} V_{ir}) \quad 4.4$$

The results of the sodium balance are summarized in Table 4.3. The amount of sodium in the 500 ml of solution prior to the beginning of the crystallization experiment is 9,10 g Na at a concentration of 18,20 g/l. Figure 4.6 shows the relationship between the cumulative mass of condensate and the calculated cumulative mass of sodium in the crystallized salt. Initially during the boiling, liquid evapourates and no crystals form. Crystals begin to crystallize out of the solution after around 29 minutes, when the volume of the remaining solution is 380 ml and the corresponding temperature 99 °C. At this point, the solution is saturated, and crystals begin to form. The boiling continues and eventually there were 2,43 g of Na in the crystals that were formed, corresponding to 6,19 g of NaCl. At this stage there was 200 ml of solution remaining in the residue and the boiling temperature of the solution was 102 °C. The residue solution was very viscous and began sputtering and so the experiment was stopped. The condensate was continuously collected was tested and contained zero sodium.

Table 4.5: The mass balance on sodium during the crystallization process. The data is the average of the three runs on the platinum refinery wastewater (sample 1)

		Residue Samples				Residue Solution		Crystals	
Time	Temperature	Volume	Na concentration	Mass of Na	Cumulative mass of Na	Volume	Mass of Na	Mass of Na	Mass NaCl
min	^{o}C	l	g/l	g	G	l	g	g	g
0	18		18,2	0,00	0,00	0,5	9,12	0,00	0,00
15	97	0,01	20,3	0,20	0,20	0,44	8,92	-0,01	-0,02
29	98	0,01	22,7	0,23	0,43	0,38	8,64	0,04	0,10
43	100	0,01	23,8	0,24	0,67	0,32	7,63	0,82	2,08
57	102	0,01	24,6	0,25	0,91	0,26	6,39	1,81	4,60
71	102	0,01	27,5	0,27	1,19	0,2	5,49	2,43	6,19

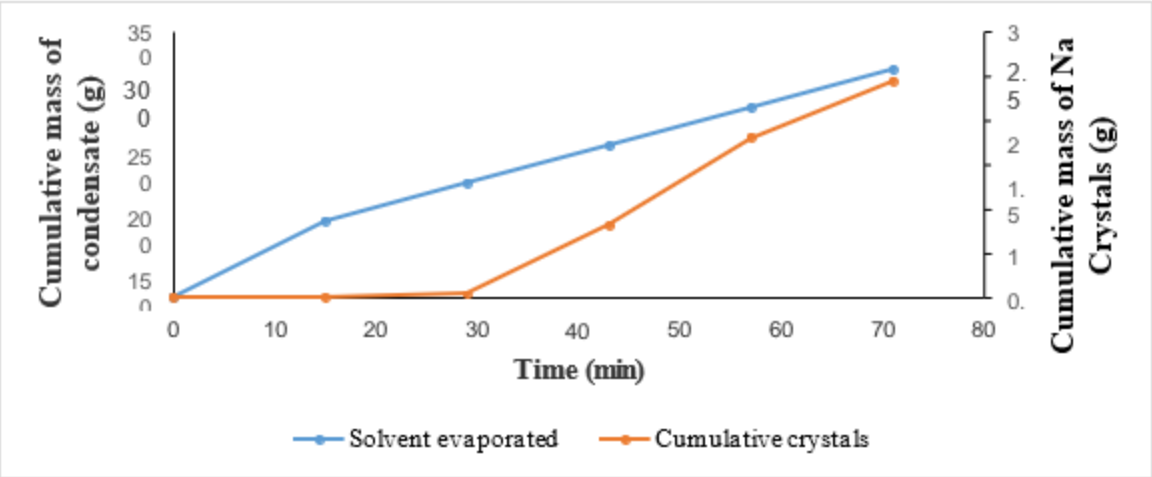

Figure 4.6: Cumulative mass of condensate and sodium in crystallized in salt vs time in batch experiments. The data is the average of the three runs on the platinum refinery wastewater.

The experiment was repeated on the synthetic wastewater sample and the results are summarized in Table 4.5. The results show that 8,52 g of NaCl is precipitated, which compares very well with the value that was determined for the wastewater sample from the platinum refinery (6,19 g).

Table 4.6: The mass balance on sodium during the crystallization process. The data is for the synthetic wastewater sample

		Residue Samples				Residue Solution		Crystals	
	Temperature	Volume	Na concentration	Mass of Na	Cumulative mass of Na	Volume	Mass of Na	Mass of Na	Mass NaCl
min	^{o}C	l	g/l	g	G	l	g	g	g
0	25		18,23	0,00	0,00	0,50	9,12	0,00	0,00
15	96	0,01	20,24	0,20	0,20	0,44	8,91	0,01	0,02
29	98	0,01	22,75	0,23	0,43	0,38	8,65	0,04	0,10
43	101	0,01	22,52	0,23	0,66	0,32	7,21	1,25	3,19
57	102	0,01	23,15	0,23	0,89	0,26	6,02	2,21	5,62
71	102	0,01	23,24	0,23	1,12	0,20	4,65	3,35	8,52

4.2.2.3 Mass balance on chloride ions

Referring to Table 4.1, the TDS (81 860 mg/l) is less than the total combined mass of chloride and sodium ions reported in the water (123 141 mg/l total). The molar ratio Na:Cl in the solution (see Table 4.2) is 1:3,7. The ratios proves that there is an excess of chloride ions in the wastewater. Thus, even if all the sodium were to precipitate, there would be 2,16 moles of chloride ions left. This gives an important insight into the behaviour of the solution during evaporative of the wastewater. HCl is volatile (vapour pressure at 298 K is 49 bar) and if the wastewater is heated, HCl will be evaporated, meaning that the concentration of chloride ions in the residue will decrease. Thus, it can expect that the condensate will be acidic.

This has quite a few implications. Firstly, the condensate will be an acidic solution, not pure water. This is not a problem, and indeed may be an advantage, if the refinery can accept the acidic condensate for recycle. As the refinery consumes both HCl and fresh water, returning the condensate to the process will reduce both the fresh water and acid consumption of the overall process, which has environmental and economic benefits. Secondly, it is required to do a chloride balance to determine how much of the chloride/chlorine is boiled off with the condensate. Unfortunately, the chloride balance was not done with the first three experimental runs that were performed on the platinum refinery wastewater (Run 1 to 3 corresponding to Tables A.2 to A.4. in Appendix A).

After the first sample of wastewater was used up, a second sample was requested in order to do the chloride balance. The second sample was analysed for chloride and sodium ions and the results are summarized in Table 4.7. It was found that although the sodium concentration was very similar in the two refinery samples, the chloride ion concentration in the second sample was nearly half that of the original (first) sample that was used.

Table 4.7: Comparison of sodium and chloride concentrations in the first and second wastewater samples of platinum refinery wastewater

	First wastewater sample from the refinery	Second wastewater sample from the refinery
Na	18 231 mg/l	18 200 mg/l
Cl	104 910 mg/l	55 000 mg/l

A full analysis of the composition of the second wastewater sample was not done because the focus was on analysing the acid concentration in the condensate. However, it is seen that if the condensate is recycled, the concentration of chloride in the recycle stream could vary, depending on the composition (acidity) of the wastewater that is treated.

The amount of salt crystals formed was determined by doing a chloride balance. If it is again assumed that no salt crystals were collected in the 10 ml samples of residue, then the total amount of chloride initially in the flask must be equal to the sum of the amount of chloride collected in the condensate, the amount of chloride in the collected samples of residue, the amount of chloride remaining in the residue solution at the end of the experiment, and the amount of chloride crystals in the boiling flask at the end of the experiment.

This can be expressed as follows:

$$C_{t^0,Cl}\, V_{t^0} = M_{c,Cl} + C_{r,Cl} V_r + \sum C_{ir,Cl}\, V_{ir} + \sum C_{ic,Cl}\, V_{ic} \qquad 4.5$$

Where:

$C_{t^0,Cl}$ and V_{t^0} are the initial concentration of chloride and volume of solution before the crystallization process respectively;

$M_{c,Cl}$ is the total mass of chloride in the crystals formed in the boiling flask;

$C_{r,Cl}$ and V_r are the final concentration of chloride and volume of solution respectively at the end of the crystallization process

$C_{ir,Cl}$ and V_{ir} are the concentration of chloride and volume of the individual sample of residue collected.

$C_{ic,Cl}$ and V_{ic} are the concentration of chloride and volume of the individual sample of condensate collected.

Equation 4.5 can be rearranged to calculate the amount of crystals formed as follows:

$$M_{c,Cl} = C_{t^0,Cl} V_{t^0} + C_{r,Cl} V_r + \sum C_{ir,Cl} V_{ir} + \sum C_{ic,Cl} V_{ic} \quad 4.6$$

The results of the chloride balance on the second platinum refinery wastewater sample are summarized in Table 4.8

Table 4.8: Chloride balance during the crystallization experiment on platinum refinery wastewater (second sample)

Time	Temperature	Condensate Samples				Residue Samples				Residue Solution		Crystals	
		Volume	Cl Conc	Mass of Cl	Cumulative mass of Cl	Volume	Cl conc	Mass of Cl	Cumulative mass of Cl	Volume	Mass of Cl	Mass of Cl	Mass NaCl
min	^{o}C	l	g/l	g	g	l	g/l	g	g	l	g	g	g
0	21				0		55	0	0	0.5	27.5	0	0
15	98	0.05	41.4	2.07	2.07	0.01	56.51	0.57	0.57	0.44	24.86	0	0
29	99	0.05	24.2	1.21	3.28	0.01	54.39	0.54	1.11	0.38	20.67	2.44	4.05
43	101	0.05	21.6	1.08	4.36	0.01	52.28	0.52	1.63	0.32	16.73	4.78	7.92
57	102	0.05	18.4	0.92	5.28	0.01	51.24	0.51	2.14	0.26	13.32	6.75	11.19
71	102	0.05	17.6	0.88	6.16	0.01	50.34	0.5	2.65	0.2	10.07	8.62	14.29

There are initially 27,5 g of chloride ions in the sample: of these 6,16 g report to the condensate and 8,62 g report to the crystals. The remaining chloride reports to the residue (10,07 g) and around 2,65 g was collected in the residue samples. Thus, the final residue has a concentration of 5 wt % HCl while the condensate has concentration of 2,5 wt % HCl.

When the mass of crystals produced in the experiments with the two different refinery wastes are compared, it is observed that the first wastewater sample produced 2,43 g of sodium in salt crystals formed which corresponds to 6,19 g of NaCl crystals. In the experiment on the second sample of waste from the refinery, the crystals contained 8,62 g chloride ions, corresponding to 14,29 g of NaCl crystals. This is hard to explain as one would have expected that less NaCl crystallized when the chloride levels were lower, due to the common ion (that is chloride) concentration being lower. However, this is not what was observed.

An experiment was also performed on the synthetic wastewater sample, as described in Chapter 3, with similar concentrations of chloride and sodium to the first refinery wastewater sample. This was to allow for a comparison to be made between the chloride concentrations and distribution between the synthetic solution which had same chloride levels as the first sample from the platinum refinery (104 910 mg/l) to that of the second sample which had a lower initial chloride concentration (55 000 mg/l).

Table 4.9: Chloride balance during the crystallization experiment on the synthesized wastewater

		Condensate Samples				Residue Samples				Residue Solution		Crystals	
Time	Temperature	Volume	Cl Conc	Mass of Cl	Cumulative mass of Cl	Volume	Cl conc	Mass of Cl	Cumulative mass of Cl	Volume	Mass of Cl	Mass of Cl	Mass NaCl
min	°C	l	g/l	g	g	l	g/l	g	g	l	g	g	g
0	21				0		106,10	0,00	0,00	0,5	53,05	0,00	0,00
15	98	0,05	154,80	7,74	7,74	0,01	100,80	1,01	1,01	0,44	44,35	-0,05	-0,08
29	99	0,05	121,40	6,07	13,81	0,01	98,00	0,98	1,99	0,38	37,24	0,01	0,02
43	101	0,05	114,40	5,72	19,53	0,01	89,50	0,90	2,88	0,32	28,64	2,00	3,31
57	102	0,05	77,20	3,86	23,39	0,01	85,90	0,86	3,74	0,26	22,33	3,58	5,94
71	102	0,05	66,60	3,33	26,72	0,01	86,60	0,87	4,61	0,2	17,32	4,40	7,30

Table 4.9 shows that the synthetic solution contained 53,05 g of chloride initially before the crystallization process commenced. In this case 26,72 g of the chloride reported to the condensate while 17,32 g of chloride remained behind in the residue. It was calculated that 4,40 g of chloride were in the precipitate which corresponds to 7,30 g of NaCl. The concentration of the condensate in this case is 10 w % HCl in condensate from the synthetic wastewater compared to 2,5 w % HCl in the condensate from the second refinery wastewater sample. Similarly, the concentration of HCl in the final residue for the synthetic wastewater was 8,6 wt % compared to the second refinery wastewater sample that was 5 wt %. The results are summarized in Table 4.10 below.

Table 4.10: Summary of calculated NaCl in residue and HCl in condensate

Sample	Concentration (g/l)			Volume of residue left (ml)	Calculated Mass NaCl in residue (g)	Concentration of HCl in Condensate (wt %)
	Na	Cl				
Refinery wastewater (Sample 1)	18 231	104 910		200	6,19	
Refinery wastewater (Sample 1)	18 200	55 000		200	14,29	2,5
Synthetic water	18 231	104 910	Na Experiment	200	8,52	
			Cl Experiment	200	7,30	10,7

4.3 Energy balance

Evaporative crystallization supplies energy to the process in order to evaporate some of the solution, resulting in the residue becoming more concentrated in the salt, and ultimately as the evaporation continues, salt crystallizes out of the residue.

The cost of energy to such a process can be considerable, depending on the process and the level of heat integration used. Two cases were considered, namely a completely heat integrated system, which corresponds to the minimum energy requirements for the process; and a process where there is no heat integration or heat recovery, which corresponds to the maximum energy requirements for the process.

To do a rough analysis to determine the order of magnitude of energy required in the two cases, had to consider a wastewater feed stream of a flowrate of 20 000 l/day and a sodium concentration of 18 231 mg/l and evaporate half of the liquid in the process, as per the procedure in the experiments. The process is represented the block diagram as below.

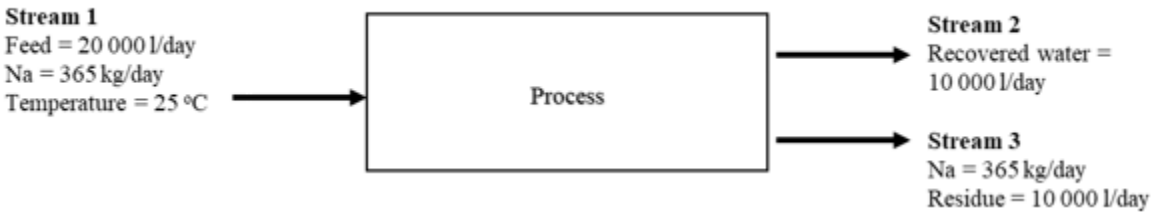

Figure 4.7: Simple diagram of evaporative crystallizer process.

4.4 Fully integrated process

It is assumed in the fully integrated process there are no heat losses. This will set the limit of performance for the equipment. In the case of a fully integrated process, the feed (stream 1) and product streams (streams 2 and 3) leave at the same temperatures, in this case ambient temperature. The recovered water will be in the liquid phase.

The energy balance for the process gives

$$\Delta H = Q \qquad 4.7$$

The only difference in enthalpy between streams 1, 2 and 3 will be the heat of crystallization and the heat effects caused by the non-ideal behaviour of acid solutions. These are fairly small effects, and thus in the limit, for a fully heat integrated evaporative crystallizer process, the energy requirements tend to zero. However, although the energy requirements are small (tending to zero) the capital costs will be large as in order to integrate the process, it would need to run reversibly, meaning temperature gradients would need to tend to zero, thus requiring large heat exchangers and many evaporative effects in series, where the evaporation occurs reversibly. This is obviously not a practical case, but how close one would want to approach this limit would depend on the cost of energy and the philosophy in terms of sustainability of processes versus cost of capital.

4.5 Process with no heat integration

In this process the heat is not recovered and so stream 2 will leave as a vapour at 102 ^{o}C while the residue will leave as a slurry, also at 102 ^{o}C. Again, the energy balance is again described by Equation 4.8. It is required to estimate the order of magnitude of the energy consumptions in the process. To this end, steam tables were used to estimate the enthalpies of the streams. The enthalpy effects caused by non-ideal behaviour of acid solution and the heats of crystallization were neglected.

From the stream tables:

$\underline{H}_1$: the specific enthalpy of liquid water at 25 ^{o}C = 105 kJ/kg

$\underline{H}_2$: the specific enthalpy of vapour at 102 ^{o}C = 2680 kJ/kg

$\underline{H}_3$: the specific enthalpy of liquid water at 102 ^{o}C = 429 kJ/kg

Thus Q = 29x10^{6} kJ/day = 336 kW.

This is the maximum energy requirements but would also correspond to the lowest capital cost in that there is no equipment to recover heat and return it to the process.

4.6 Implications for recovering water

The refinery is currently disposing of around 20 000 l/day via sending this material to landfill. Half of the volume of the acidic wastewater stream can be recovered and returned back to the refinery. Thus 10 000 l/day could be returned to the process which will reduce the freshwater consumption of the process by 10 000 l/day. Furthermore, this will reduce the volume of waste going to disposal by a half, namely only 10 000 l/daywill need to be disposed of.

The amount of Cl that can be recovered is variable and depends on the quantity of chloride in the waste. In the two samples that were investigated, recovery rates were between a 2,5 w% and 10,7 wt% aqueous HCl solution. This corresponds to a saving of between 250 to 1000 kg/day of HCl. As the concentration of the recovered solution is variable, the recycling process would need to monitor the composition of the recycled stream and make up the acid concentration to some fixed value for reuse in the prices.

The choice of how much energy integration to do will depend on many factors. If there is waste heat available (a quantity of 336kW) in either the refinery or any other part of the mining operation, then the choice might be to use the waste heat and not to do heat recovery and integration. This would lead to the simplest and cheapest process and would utilize a waste heat source.

Alternatively, the evaporation could be done in multiple effects, which would decrease the energy consumption of the process but would increase the capital cost. The vapour from first effect is separated and sends to the second effect in order boil the effluent and so as to third effect. Roughly speaking as shown in Figure 4.8, the energy consumption of the process is inversely proportional to the number of stages. However, the capital cost would be closer to proportional to the number of stages, as the peripherals such as controllers, values, instrumentation etc. would be the same for each evaporative effect. However, the cost of each stage could be scaled by the 2/3 rule, as the vapour flow per stage would be smaller with more stages. The calculated relative cost of the process as a function of number of stages is shown in Table 4-11.

Table 4.11: Number of stages in relation to relative capital cost and energy

Stages	Energy (kW)	Relative Vapour Flow per stage	Relative cost per stage	Relative cost for process
1	336	1	1,00	1,00
2	168	0,5	0,63	1,26
3	112	0,33	0,48	1,44
4	84	0,25	0,40	1,59
5	67.2	0,2	0,34	1,71

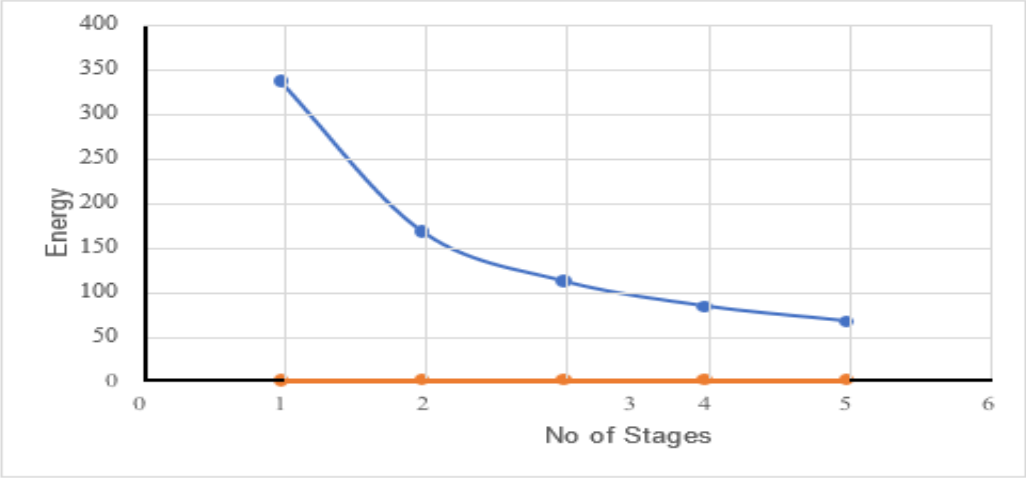

Figure 4.8: Effect of Number of stages vs energy required and relative capital cost.

A multiple effect evaporative crystallizer consists of a set of single direction evaporative crystallizers, where each effect corresponds to an evaporative crystallizer. During operation, the steam produced in the first effect is used as heating steam in the second effect, and so on. This configuration can increase the economy of the process. As the temperature decreases in each successive stage evaporation continues because the pressure and boiling point are also reduced. The use of each additional effect increases the energy efficiency of the system.

The recovered condensate is acidic and therefore the materials of construction would need to be very carefully chosen and this would obviously impact on capital costs. Technologies such as multistage vapour compression may be difficult to implement due to materials of construction limitations and thus the balance between capital cost and energy saving would need to be made carefully, balancing cost of capital, operating costs and the importance of recovering water, thereby reducing water consumption and making the process more environmentally sustainable.

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

There is a growing drive to reduce the environmental impact of processes, thereby making them more sustainable. To this end there is a need to reduce the waste produced by processes. One of the ways to achieve this is to try and recover material that would otherwise be dumped to the environment and rather recycle it back to the process. This not only reduces the amount of waste material but also reduces the amount of material fed to the process.

South Africa is a water stressed country and there is pressure to reduce water consumption. Thus, it is important to try and recover water that would otherwise be disposed of to the environment and rather recycle and thereby reduce water consumption. The study considered a wastewater stream from a platinum refinery. The waste is currently neutralized and disposed of to landfill. It was considered whether water could be recovered from this process by use of evaporative crystallization. The major impurities in the wastewater are sodium, with a concentration 18 231 mg/l and chloride. Two different samples of wastewater were tested from the refinery, and it was observed that although the sodium concentrations were nearly the same in the two samples, the chloride concentrations differed by nearly a factor of 2 with chloride concentrations of 55 000 mg/l and 104 910 mg/l in the two samples, respectively. A synthetic solution with a sodium concentration of 18 231 mg/l and a chloride concentration of 104 910 mg/l was also prepared to compare the effects of other ions and impurities in the wastewater.

It was found that about half of the water in the waste could be recovered in the condensate. Chloride from the wastewater was also recovered in the condensate. The study observed that the recovery of the chloride depended on the amount of chloride in the wastewater. The other ions and impurities in the wastewater did not have a significant effect on the process and the synthetic wastewater and the wastewater from the refinery behaved in a similar manner.

Thus, the study proposes that the acid condensate could be recovered and recycled to the process.

If 20 000 l/day of wastewater is treated, this would lead to a reduction in water consumption of 10 000 l/day, reducing in HCl consumption of between 250 kg/day to 1000 kg/day and a reduction of 10 000 l/day of residue being disposed of to waste.

A decision that would need to be made is how much capital would need to be spent in order to reduce energy consumption. The simplest one stage process, where there is no energy recovery, would require a heat input of 336 kW at a temperature greater than 102 ^{o}C. By adding more evaporative-effects and doing more heat recovery and integration, in the limit the energy consumption could be reduce to close to 0. This however comes at the costs of a very high (infinite) capital cost. The optimum between capital cost and energy saving would depend on whether there was waste heat available or not, the drive to reduce water consumption in the process and the return on investment (ROI) required by the company.

The objective of the study was to efficiently remove sodium and chloride ions from platinum refinery wastewater and produce reusable water. But ultimately the solvent that was produced was a hydrochloric acid as condensate and a sodium chloride concentrated solution. The acid can be recycled back to the process and this could result in zero liquid discharge process.

5.2 Recommendations

It is recommended that further investigation to be done to quantify and characterize the sludge from the solution, and separation process that is economically efficient. Furthermore, opportunities to recycle HCl back to the refinery would need to be done but this would require process information. Renewable energy should be incorporated in the design as the source of energy in future.

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APPENDIX A

Table A. 1: Full analysis of platinum refinery wastewater used in this research

Wastewater analysis

Sample name			**Before Treatment**
Sample date			**Unknown**
Sample container description			**Glass Container**
Submission date			**2013/02/01**
Sample type			**Water**
Set Point ID			
Visual inspection			**N/A**
Method no			
Chemical Properties and Parameters		**Unit**	
M464	**Ammonia Nitrogen**	**mg/L**	**<0.1**

#	**Bicarbonate Alkalinity**	**mg/L CaCO3**	**<10**
#	**Bromide**	**mg/L**	**<0.5**
#	**Carbonate Alkalinity**	**mg/L CaCO3**	**<10**
#	**Chemical Oxygen Demand (COD)**	**mg/L**	**11800**
M469	**Chloride**	**mg/L**	**104910**
M461	**Conductivity**	**mS/m @ 25°C**	**>20000**
M475	**Fluoride**	**mg/L**	**<0.1**
M471	**Hexavalent Chromium (Cr VI)**	**mg/L**	**0.093**
M465	**Nitrate Nitrogen**	**mg/L N**	**<0.1**
M466	**Nitrite Nitrogen**	**mg/L N**	**<0.1**

#	**Oil & Grease**	**mg/L**	**<10**
M468	**Orthophosphate**	**mg/L P**	**0.1**
M460	**pH**	**-**	**<0.2**
#	**Phenolphthalein Alkalinity**	**mg/L CaCO3**	**<10**
#	**Phenols**	**mg/L**	**0.15**
M476	**Sulphate**	**mg/L**	**236**
#	**Sulphides**	**mg/L**	**<0.5**
M463	**Total Alkalinity**	**mg/L CaCO3**	**<10**
#	**Total Cyanide**	**mg/L**	**<0.05**
#	**Total Dissolved Solids**	**mg/L @ 180°C**	**81860**

#	**Total Hardness**	**mg/L CaCO3**	**76**
#	**Total Kjeldahl Nitrogen**	**mg/L N**	**12.5**
#	**Total Phosphorus**	**mg/L P**	**<1**
#	**Total Suspended Solids**	**mg/L**	**84**
#	**Turbidity**	**NTU**	**39.4**
M474	**Aluminium (Al)**	**mg/l**	**3.19**
M474	**Antimony (Sb)**	**mg/l**	**0.09**
M474	**Arsenic (As)**	**mg/l**	**0.43**
M474	**Barium (Ba)**	**mg/l**	**0.08**
M474	**Beryllium (Be)**	**mg/l**	**<0.02**
#	**Bismuth (Bi)**	**mg/l**	**0.2**
M474	**Cadmium (Cd)**	**mg/l**	**<0.02**

M474	**Calcium (Ca)**	**mg/l**	**15.9**
M474	**Chromium (Cr)**	**mg/l**	**1.19**
M474	**Cobalt (Co)**	**mg/l**	**0.3**
M474	**Copper (Cu)**	**mg/l**	**6.78**
#	**Gallium (Ga)**	**mg/l**	**0.47**
#	**Indium (In)**	**mg/l**	**0.06**
M474	**Iron (Fe)**	**mg/l**	**4008**
M474	**Lead (Pb)**	**mg/l**	**0.81**
#	**Lithium (Li)**	**mg/l**	**<0.04**
M474	**Magnesium (Mg)**	**mg/l**	**8.78**
M474	**Manganese (Mn)**	**mg/l**	**20.1**
M474	**Mercury (Hg)**	**mg/l**	**<0.50**
M474	**Molybdenum (Mo)**	**mg/l**	**0.03**

M474	**Nickel (Ni)**	**mg/l**	**25.2**
#	**Niobium (Nb)**	**mg/l**	**<0.04**
#	**Palladium (Pd)**	**mg/l**	**<0.02**
M474	**Platinum (Pt)**	**mg/l**	**4**
M474	**Potassium (K)**	**mg/l**	**13.06**
M474	**Ruthenium (Ru)**	**mg/l**	**0.53**
M474	**Scandium (Sc)**	**mg/l**	**<0.04**
M474	**Selenium (Se)**	**mg/l**	**2.33**
M474	**Silicon (Si)**	**mg/l**	**13.74**
M474	**Silver (Ag)**	**mg/l**	**9.22**
M474	**Sodium (Na)**	**mg/l**	**18231**
M474	**Strontium (Sr)**	**mg/l**	**0.1**
#	**Sulphur (S)**	**mg/l**	**95.1**

#	**Tantalum (Ta)**	**mg/l**	**0.03**
#	**Tellurium (Te)**	**mg/l**	**1.56**
#	**Thallium (Tl)**	**mg/l**	**<0.04**
M474	**Thorium (Th)**	**mg/l**	**0.03**
M474	**Tin (Sn)**	**mg/l**	**0.21**
#	**Titanium (Ti)**	**mg/l**	**0.05**
#	**Tungsten (W)**	**mg/l**	**<0.04**
M474	**Uranium (U)**	**mg/l**	**<0.04**
M474	**Vanadium (V)**	**mg/l**	**0.4**
#	**Yttrium (Y)**	**mg/l**	**<0.02**
M474	**Zinc (Zn)**	**mg/l**	**44.72**
#	**Zirconium (Zr)**	**mg/l**	**0.08**

Table A. 1: Run 1 of platinum refinery wastewater

Volume Residue	Temperature	Time	Sodium Concentration in Residue	
ml	^{0}C	min	(g/l)	(mol/l)
500	18	0	18.23	0.79
440	97	15	20.27	0.88
380	98	29	22.71	0.99
320	100	43	23.82	1.04
260	102	57	24.60	1.07
200	102	71	27.47	1.19

Table A. 2: Run 2 of platinum refinery wastewater

Volume Residue	Temperature	Time	Sodium Concentration in Residue	
ml	^{0}C	min	(g/l)	(mol/l)
500	21	0	18.23	0.79
440	97	15	20.28	0.88
380	98	29	22.76	0.99
320	100	43	23.87	1.04
260	102	57	24.61	1.07
200	102	71	27.37	1.19

Table A. 3 Run 3 of platinum refinery wastewater

Volume Residue	Temperature	Time	Sodium Concentration in Residue	
ml	^{0}C	min	(g/l)	(mol/l)
500	21	0	18.23	0.79
440	98	15	20.26	0.88
360	99	29	22.77	0.99
320	101	43	23.84	1.04
260	102	57	24.55	1.07
200	102	71	27.55	1.20

Table A. 4: Synthesized platinum refinery wastewater with no other impurities

Volume Residue	Volume Residue	Time	Sodium Concentration in Residue	
ml	^{0}C	min	(g/l)	(mol/l)
500	25	0	18.2	0.79
440	96	15	23.3	1.01
380	98	29	25.8	1.12
320	101	43	26.9	1.17
260	102	57	28.7	1.25
200	102	71	28.8	1.25

Table A. 6: Chloride in synthesized wastewater

Time	Temperature	Chloride Concentration in Condensate		Chloride Concentration in Residue	
min	°C	g/l	mol/l	g/l	mol/l
0	21			106.1	3.01
15	98	154.8	4.39	100.8	2.86
29	99	121.4	3.44	98.0	2.78
43	101	114.4	3.24	89.5	2.54
57	102	77.2	2.19	85.9	2.43
71	102	66.6	1.89	86.6	2.45